General introduction to rare earths

Koen Binnemans

KU Leuven - University of Leuven (Belgium)

What do chemistry textbooks tell us about rare earths or lanthanides?

- *"Lanthanum has only one important oxidation state in aqueous solution, the +3 state. With few exceptions, this tells the whole boring story about the other lanthanides."*

  Ref. G.C. Pimentel, R.D. Sprately, *Understanding Chemistry*; Holden-Day, 1971, San Francisco, CA, p. 862.

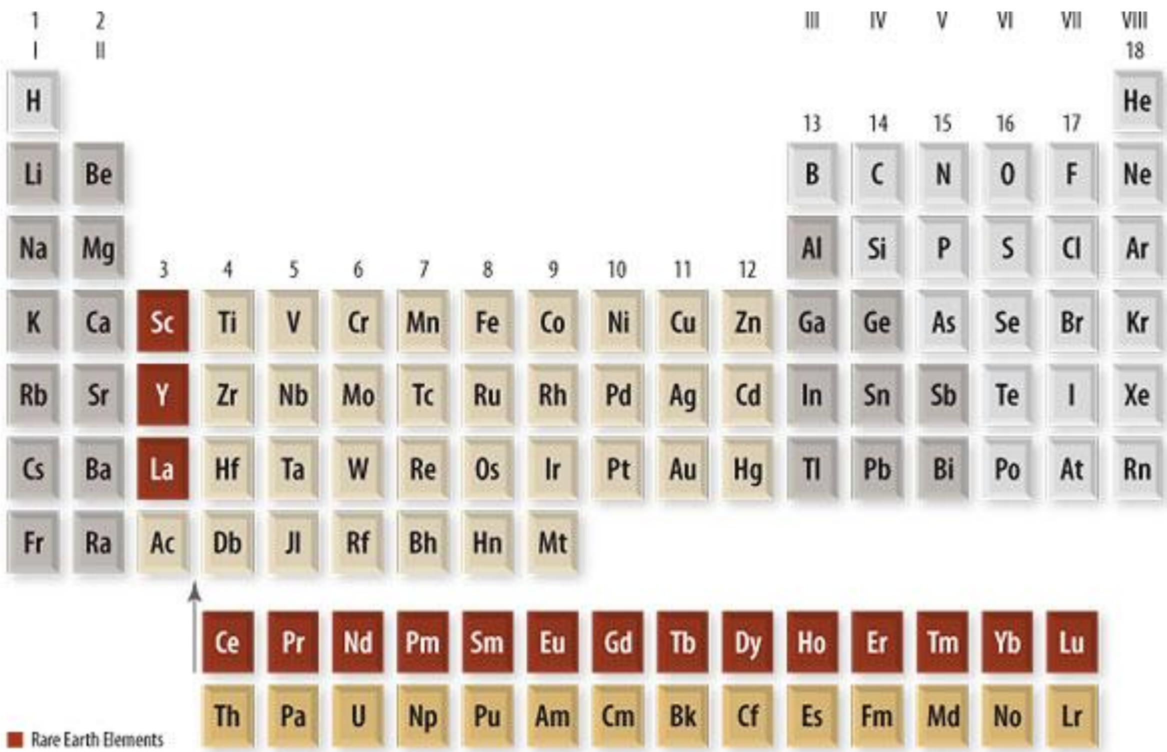
- *"Names of the lanthanides (praseodymium, dysprosium, ytterbium,…) are ugly and confusing".*

  Ref.: E.G. Marks, J. Marks, *Found. Chem.* 12 (2010) 85–93.

- *"Cramming all the lanthanides together in one box of group III of PSE creates perception that these elements are very boring from a chemical point of view."*

  Ref.: W.B. Jensen, *Comp. & Maths. with Appls.* 12B (1986) 487-510.

Rare earths in the periodic table



Lanthanides = series of elements La-Lu

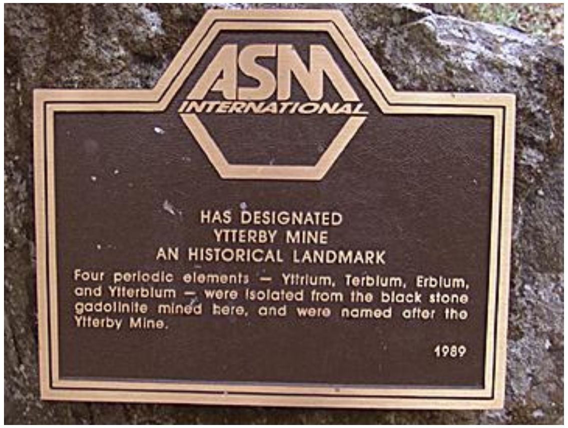
Rare earths = lanthanides + Y + Sc

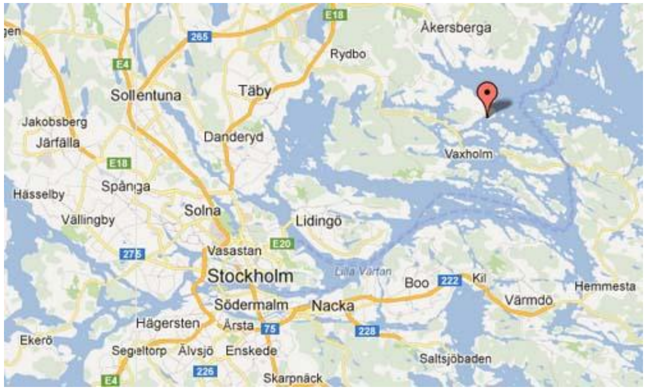
REEs = rare-earth elements

Rare earths: names and symbols

Name	Chemical Symbol	Atomic Number (Z)
Scandium	Sc	21
Yttrium	Y	39
Lanthanum	La	57
Cerium	Ce	58
Praseodymium	Pr	59
Neodymium	Nd	60
Promethium	Pm	61
Samarium	Sm	62
Europium	Eu	63
Gadolinium	Gd	64
Terbium	Tb	65
Dysprosium	Dy	66
Holmium	Ho	67
Erbium	Er	68
Thulium	Tm	69
Ytterbium	Yb	70
Lutetium	Lu	71

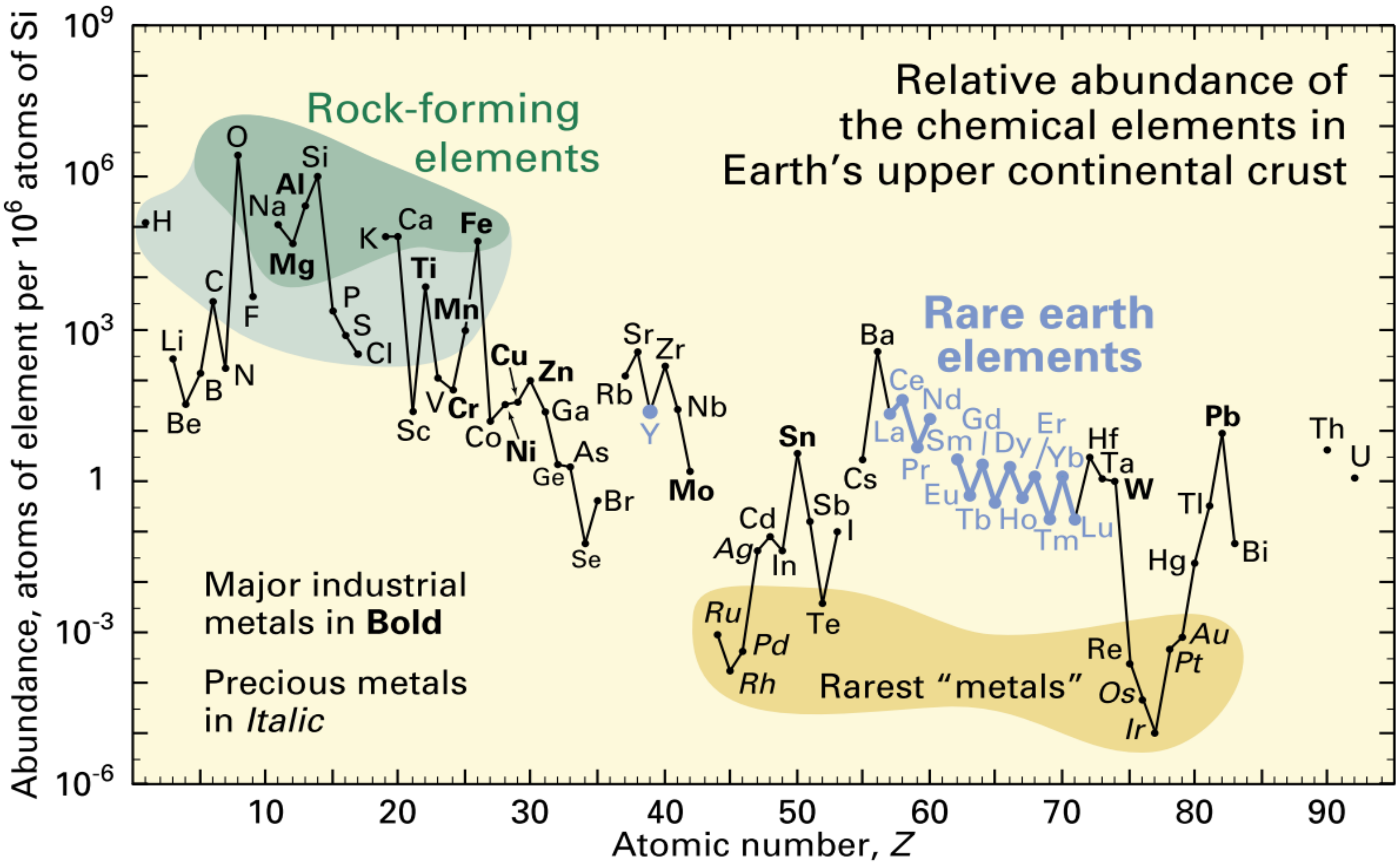
Ytterby (Sweden)





Rare earths: How do they look like?

Rare earths are not rare!



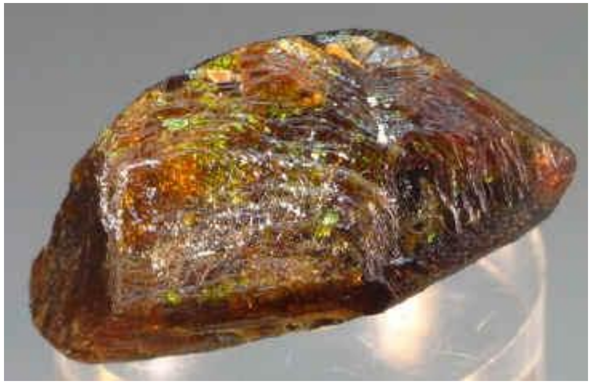
Source: US Geological Survey

Rare-earth ore minerals

Carbonate Minerals	Bastnäsite	$(Ce,La)(CO_3)F$
Phosphate Minerals	Monazite	$(Ce,La,Nd,Th)PO_4$
	Xenotime	YPO_4
	Apatite	$Ca_5(PO_4)_3(F,Cl,OH)$
Oxidic/ Alkaline Minerals	Eudialyte	$Na_4(Ca,Ce)_2(Fe^{2+},Mn,Y)ZrSi_8O_{22}(OH,Cl)_2$
	Allanite	$(Ce,Ca,Y)_2(Al,Fe^{3+})_3(SiO_4)_3OH$
	Loparite	$(Ce,La,Na,Ca,Sr)(Ti,Nb)O_3$

Bastnäsite $(Ce,La)(CO_3)F$

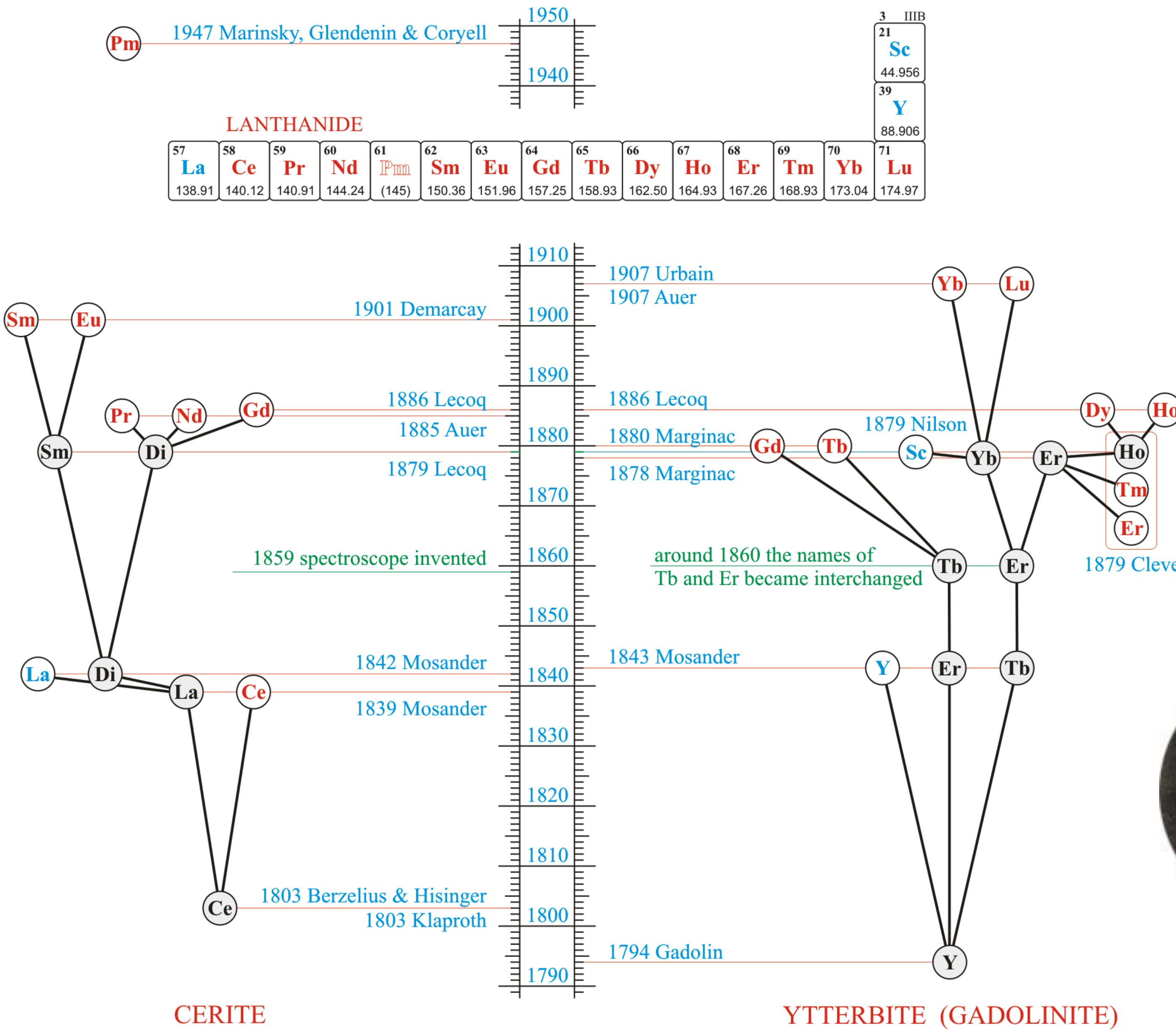
Monazite (Ce,La,Nd,Th)PO_4



Rare-earth separation problem

- Rare earths occur as mixtures in nature
- Many applications require pure rare earths
- Mixtures are difficult to separate due to similarities in chemical properties of rare earths
- Separation of rare earths is one of the most difficult separations in inorganic chemistry
- Separation is done on an industrial scale by solvent extraction (SX)

SHORT HISTORY OF RARE EARTH ELEMENTS



Johan Gadolin

Source: http://www.periodni.com

Chemical properties

- Similar chemical properties, with a gradual change across the lanthanide series (**lanthanide contraction**)
- Chemistry is dominated by the +3 oxidation state (trivalent ions) exceptions because of stability of empty, half-filled or filled f-orbitals

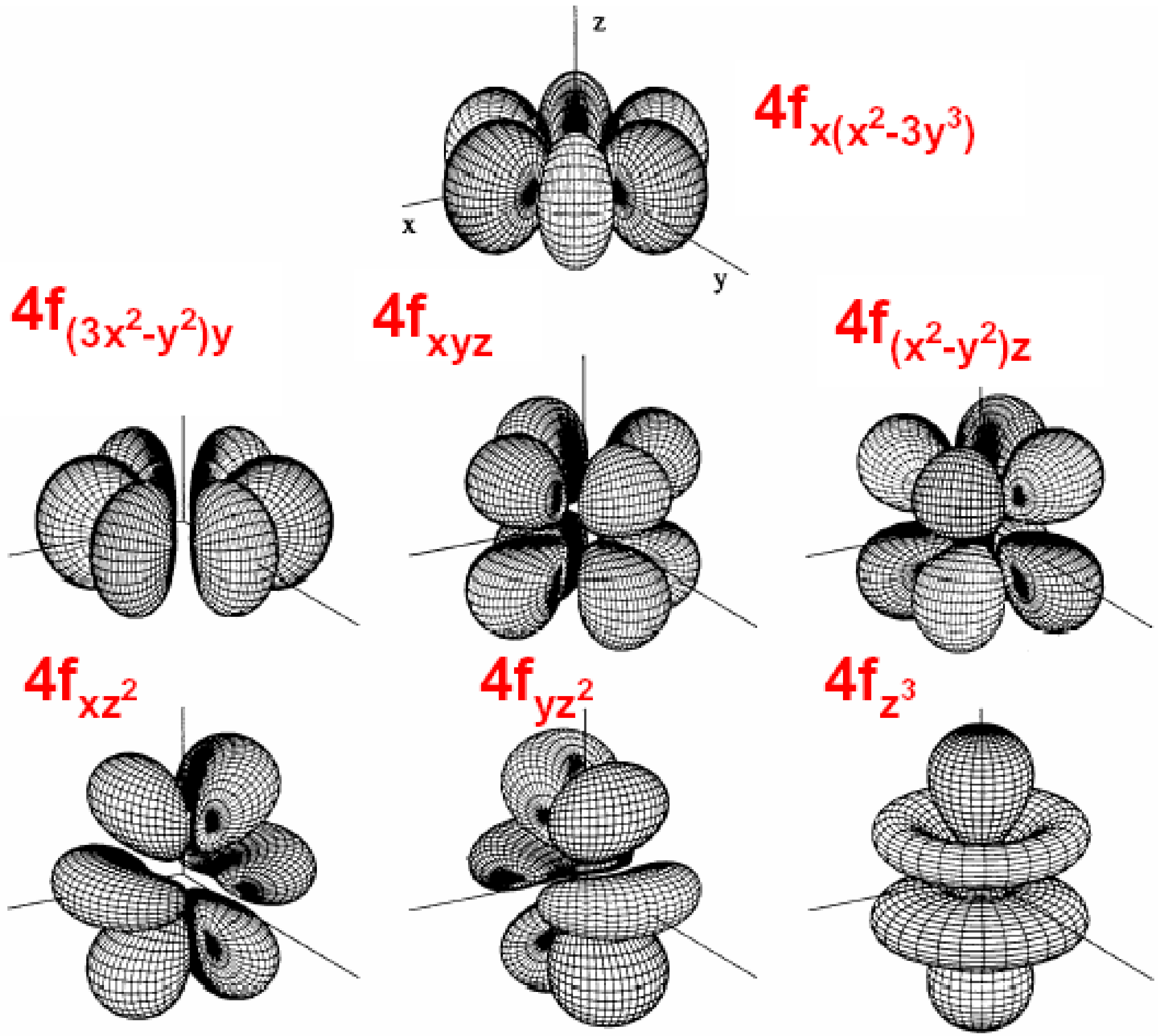
  Ce^{4+} Eu^{2+} Yb^{2+}
- Chemical bonding is mainly ionic, very limited covalent effects
- Fast ligand exchange in solution (kinetically labile)
- Ln^{3+} ions are hard Lewis acids
- Preference for binding O-donor ligands
- Complex formation with water molecules is very common Hydrated compounds are often formed
- Stable complexes with polydentate ligands (e.g. EDTA)
- Aqua ions hydrolyze: increasingly so from La to Lu

$$[Ln(H_2O)_n]^{3+} + H_2O \rightarrow [Ln(H_2O)_{n-1}(OH)]^{2+} + H_3O^+$$

Chemical properties II

- High coordination numbers: most often 8 of 9, but up to 12
- Coordination polyhedra are determined by steric factors, not by orbital overlap
- Coordination polyhedra are often ill-defined
- Gradual filling of the 4f orbitals across the lanthanide series
- 4f electrons well shielded from the environment by closed $5s^2$ and $5p^6$ shells
- 4f orbitals do not participate in chemical bonding
- Ligand field effects are small compared to d-block elements
  Atomic-like absorption and emission spectra (narrow lines or bands)
- Pale colours from weak, narrow forbidden f-f optical transitions.
- Magnetic and optical properties are largely independent of environment (e.g. similar spectra in gas/solution/solid).
- Rare earths have unique electronic and magnetic properties
  very important for applications of rare earths

4f-orbitals



Configurations of rare-earth ground states

Element	Neutral Atom Configuration	
Sc		$3d4s^2$
Y		$4d5s^2$
La	$4f^0$	$5d6s^2$
Ce	$4f^1$	$5d6s^2$
Pr	$4f^3$	$6s^2$
Nd	$4f^4$	$6s^2$
Pm	$4f^5$	$6s^2$
Sm	$4f^6$	$6s^2$
Eu	$4f^7$	$6s^2$
Gd	$4f^7$	$5d6s^2$
Tb	$4f^9$	$6s^2$
Dy	$4f^{10}$	$6s^2$
Ho	$4f^{11}$	$6s^2$
Er	$4f^{12}$	$6s^2$
Tm	$4f^{13}$	$6s^2$
Yb	$4f^{14}$	$6s^2$
Lu	$4f^{14}$	$5d6s^2$

- Displayed on periodic tables and in many textbooks
- Generally not important to most scientists – who work with solids or liquids
- Important in chemical thermodynamic cycles if the $Ln_{(g)}$ gas state is involved

Electronic configurations of Ln^{3+} ions: filling of 4f orbitals

Table 9.14 Names, symbols, and properties of the lanthanides

Z	Name	Symbol	Configuration of M^{3+}	$E^{\ominus}/V$	$r(M^{3+})/\text{Å}$*	O.N.†
57	Lanthanum	La	[Xe]	−2.38	1.16	**3**
58	Cerium	Ce	$[Xe]4f^1$	−2.34	1.14	**3**, 4
59	Praseodymium	Pr	$[Xe]4f^2$	−2.35	1.13	**3**, 4
60	Neodymium	Nd	$[Xe]4f^3$	−2.32	1.11	2(n), **3**
61	Promethium	Pm	$[Xe]4f^4$	−2.29	1.09	**3**
62	Samarium	Sm	$[Xe]4f^5$	−2.30	1.08	2(n), **3**
63	Europium	Eu	$[Xe]4f^6$	−1.99	1.07	2(a), **3**
64	Gadolinium	Gd	$[Xe]4f^7$	−2.28	1.05	**3**
65	Terbium	Tb	$[Xe]4f^8$	−2.31	1.04	**3**, 4
66	Dysprosium	Dy	$[Xe]4f^9$	−2.29	1.03	2(n), **3**
67	Holmium	Ho	$[Xe]4f^{10}$	−2.33	1.02	**3**
68	Erbium	Er	$[Xe]4f^{11}$	−2.32	1.00	**3**
69	Thulium	Tm	$[Xe]4f^{12}$	−2.32	0.99	2(n), **3**
70	Ytterbium	Yb	$[Xe]4f^{13}$	−2.22	0.99	2(a), **3**
71	Lutetium	Lu	$[Xe]4f^{14}$	−2.30	0.98	**3**

*Ionic radii for C.N. = 8 from R.D. Shannon, *Acta Crystallogr.* **A32**, 751 (1976).
†Oxidation numbers in bold type indicate the most stable states; other states that can be achieved in aqueous (a) and nonaqueous (n) solution are also included.

Why are Ln^{3+}_{aq} ions so stable?

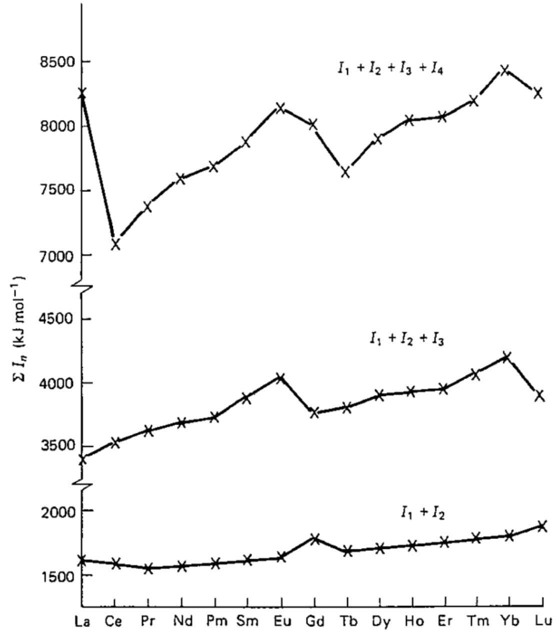
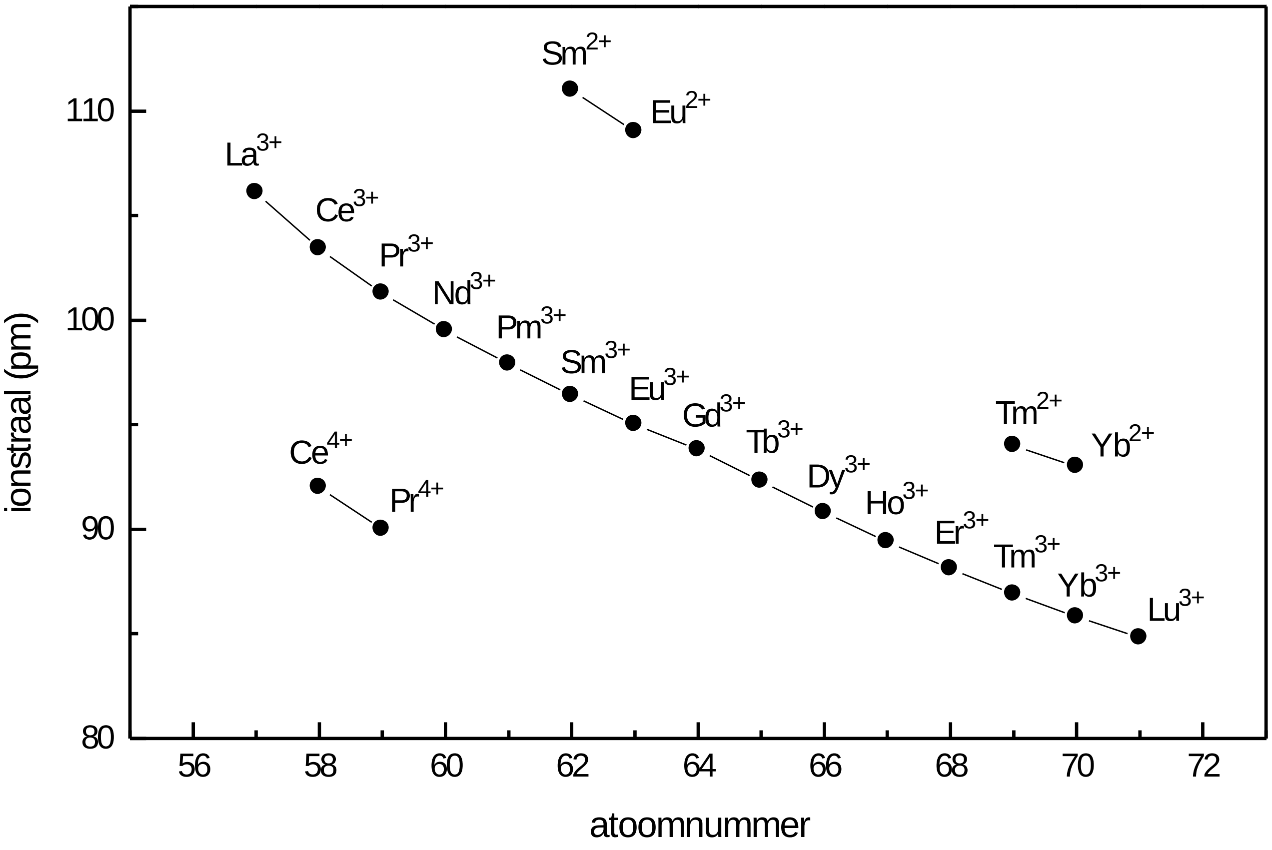


Figure 2.3
Cumulative ionization energies across the lanthanide Series (reproduced by permission of Macmillan from S.A. Cotton, *Lanthanides and Actinides*, Macmillan, 1991).

Table 2.4 Enthalpies of hydration of the lanthanide ions (values given as $-\Delta H$ hydr/kj mol^{-1}

La^{3+}	Ce^{3+}	Pr^{3+}	Nd^{3+}	Pm^{3+}	Sm^{3+}	Eu^{3+}	Gd^{3+}	Tb^{3+}	Dy^{3+}	Ho^{3+}	Er^{3+}	Tm^{3+}	Yb^{3+}	Lu^{3+}	Y^{3+}
3278	3326	3373	3403	3427	3449	3501	3517	3559	3567	3623	3637	3664	3706	3722	3583
	Ce^{4+}				Sm^{2+}	Eu^{2+}							Yb^{2+}		
	6309				1444	1458							1594		

Lanthanide contraction



Tetravalent lanthanides

- **Ce, Pr, Nd** and **Tb** may have +4 oxidation state
  E^0_{red} for $Ln^{4+}(aq) + e^- \leftrightarrows Ln^{3+}(aq)$ in acidic solutions:
  +1.72 V for Ce^{4+}, stable in water
  +3.20 V for Pr^{4+}, oxidizes water
  +3.10 V for Tb^{4+}, oxidizes water
- Many examples of Ce^{4+} compounds are known
- Ce^{4+} is used as oxidant for redox titrations and in organic synthesis (1 electron oxidant)
- Tb^{4+} has been reported as carbonato complexes in water
- Pr^{4+} and Nd^{4+} compounds are only known in the solid state, including in mixed-valence oxides Pr_6O_{11} and Tb_4O_7.

Tetravalent cerium salts

Ceric ammonium nitrate

$(NH_4)_2[Ce(NO_3)_6]$

Ceric ammonium sulfate

$(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O$

Divalent lanthanides

- **Sm**, **Eu**, and **Yb** have a relatively stable +2 state

E^{0}_{red} for $Ln^{3+}(aq) + e^- \leftrightarrows Ln^{2+}(aq)$ in acidic solutions:

-0.35 V for Eu^{2+}, stable in water

-1.15 V for Yb^{2+}, reduces water

-1.56 V for Sm^{2+}, reduces water

Divalent lanthanides

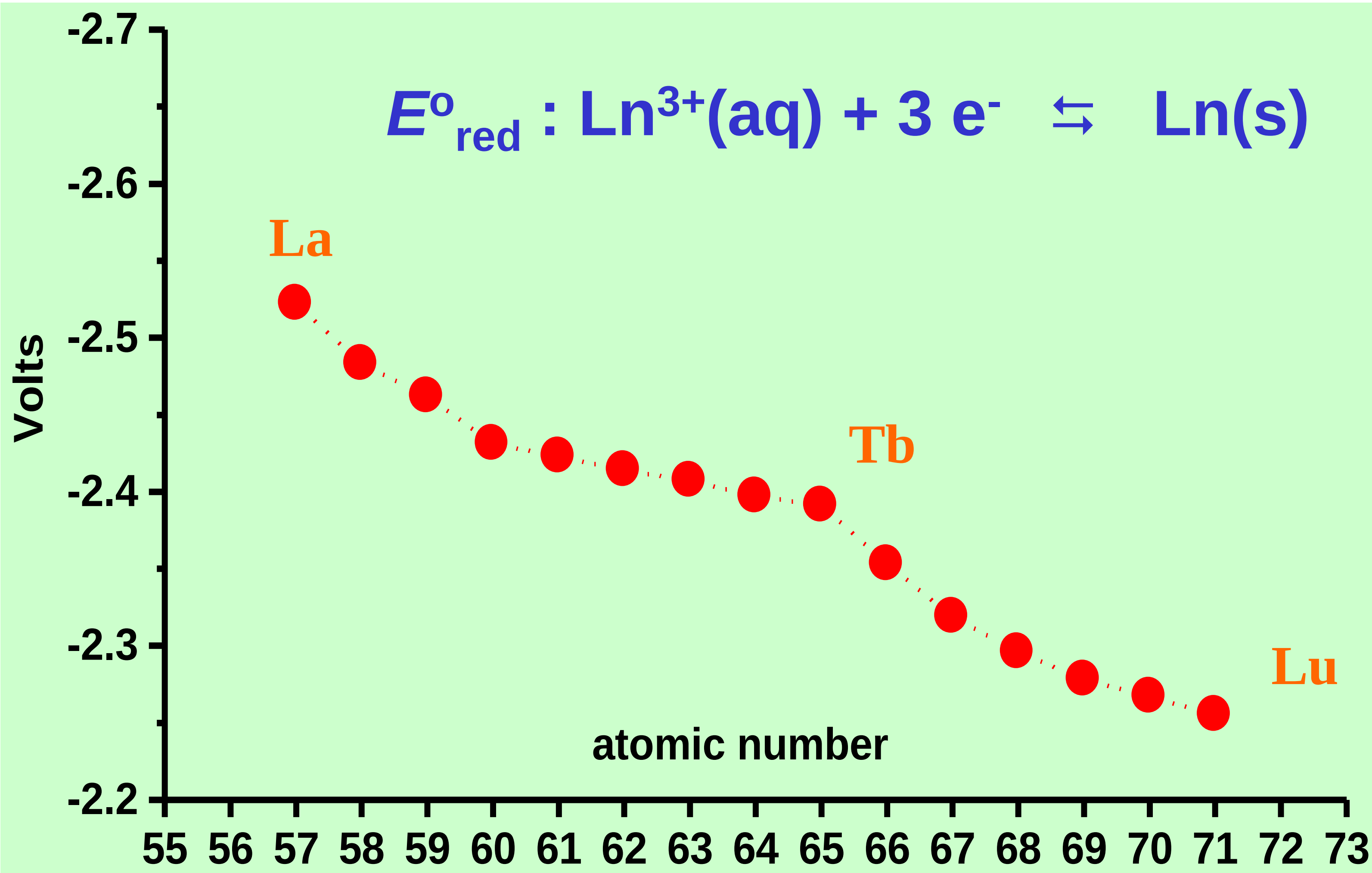
- Tm(II), Nd(II), Dy(II), Er(II), Ho(II), Pr(II), are known in the solid state and/or in non-aqueous solvents

Table 1
Ln(III)/Ln(II) reduction potentials (versus NHE) in order of increasing reducing power [5] and the electron configurations of the Ln(II) reductant

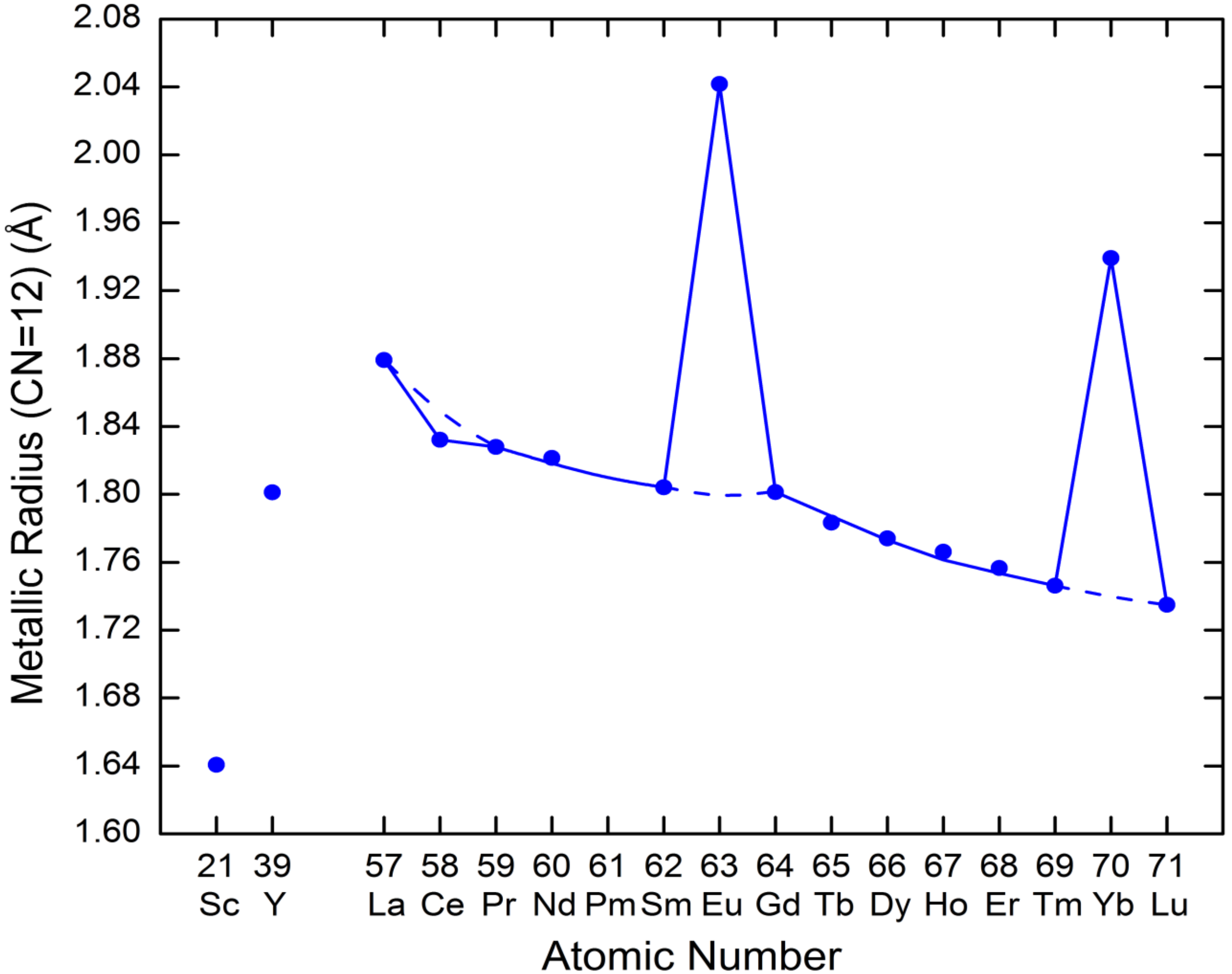
Eu	−0.35 V	[Xe]$4f^7$	Ho	−2.9 V	[Xe]$4f^{11}$
Yb	−1.15 V	[Xe]$4f^{14}$	La	−3.1 V	[Xe]$4f^1$
Sm	−1.55 V	[Xe]$4f^6$	Er	−3.1 V	[Xe]$4f^{12}$
Tm	−2.3 V	[Xe]$4f^{13}$	Ce	−3.2 V	[Xe]$4f^2$
Nd	−2.6 V	[Xe]$4f^4$	Tb	−3.7 V	[Xe]$4f^9$
Dy	−2.6 V	[Xe]$4f^{10}$	Gd	−3.9 V	[Xe]$4f^8$
Pr	−2.7 V	[Xe]$4f^3$			

W.J. Evans, *Coord. Chem. Rev.* 206-207 (2000) 263-283

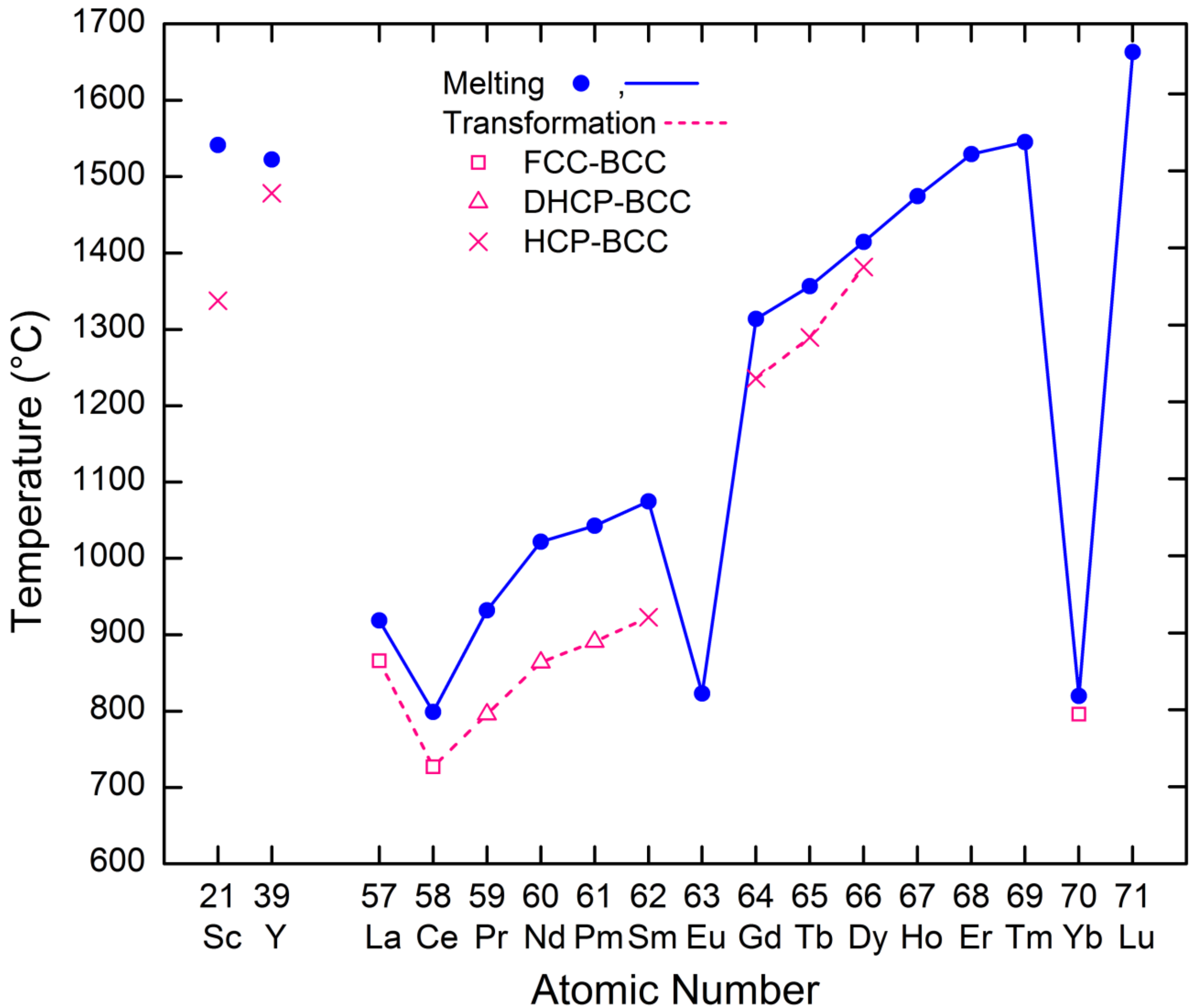
Reduction to rare-earth metals



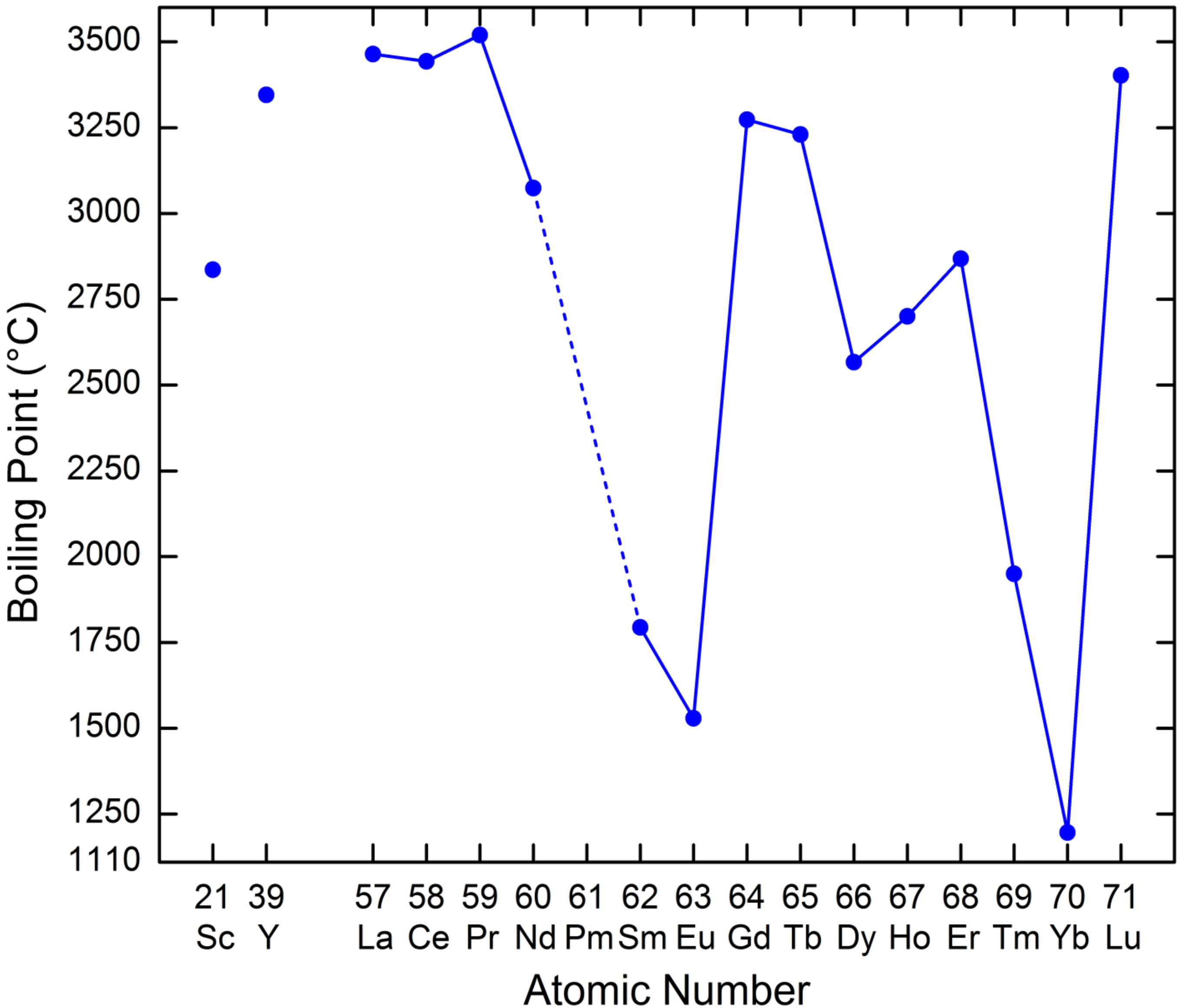
Metallic radius of rare-earth metals



Melting points and transformation temperatures of rare-earth metals



Boiling point of rare-earth metals



Rare-earth oxides

- Normal Oxides – Sesquioxide R_2O_3

  Among the most stable oxides

- Other Valence State Oxides

  Tetravalent or partially tetravalent

  CeO_2 all 4+

  Pr_6O_{11} $4PrO_2 + Pr_2O_3$

  Tb_4O_7 $2TbO_2 + Tb_2O_3$

  Divalent or partially divalent

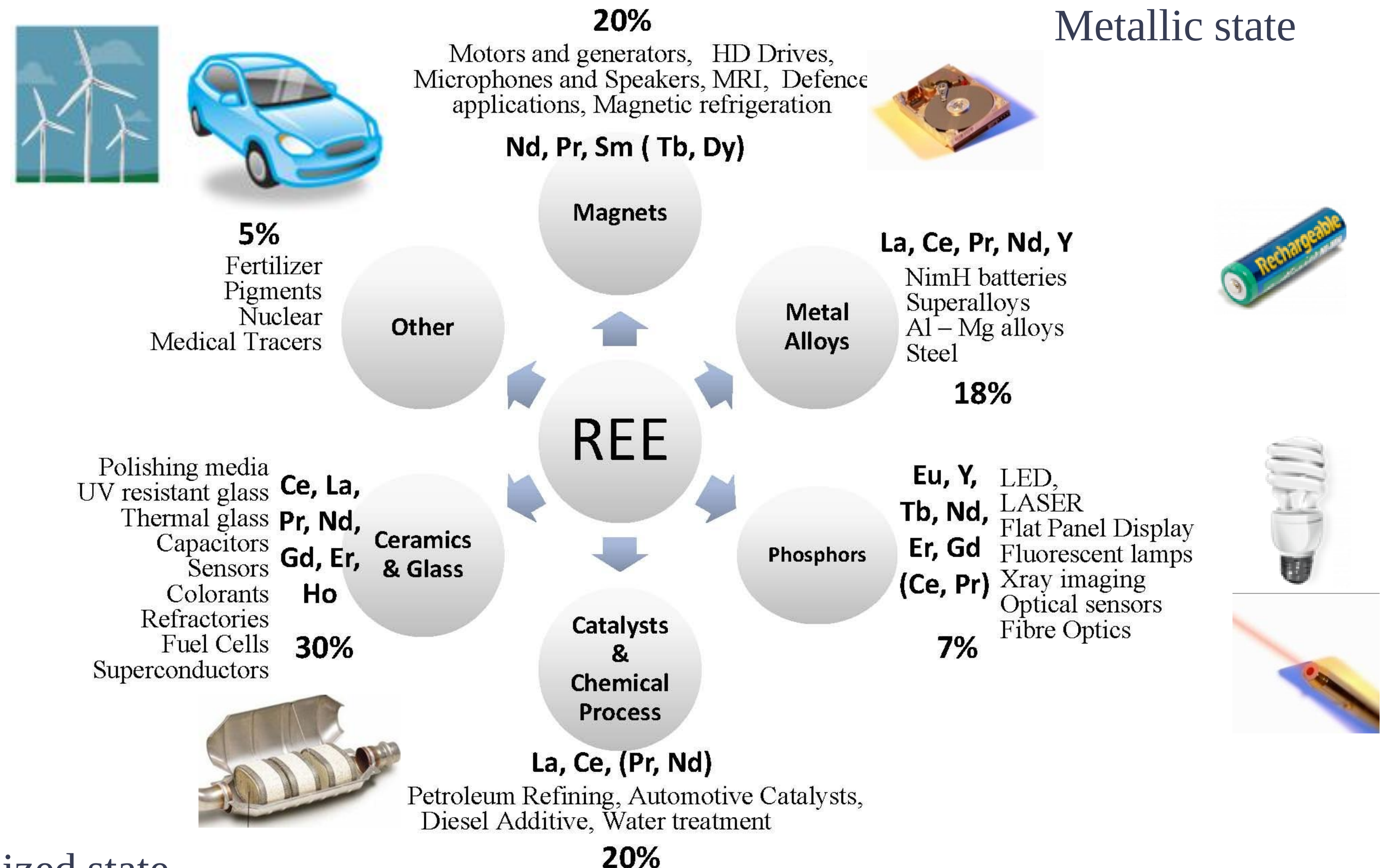
  EuO 2+

  Eu_3O_4 $EuO + Eu_2O_3$

Pr_6O_{11}

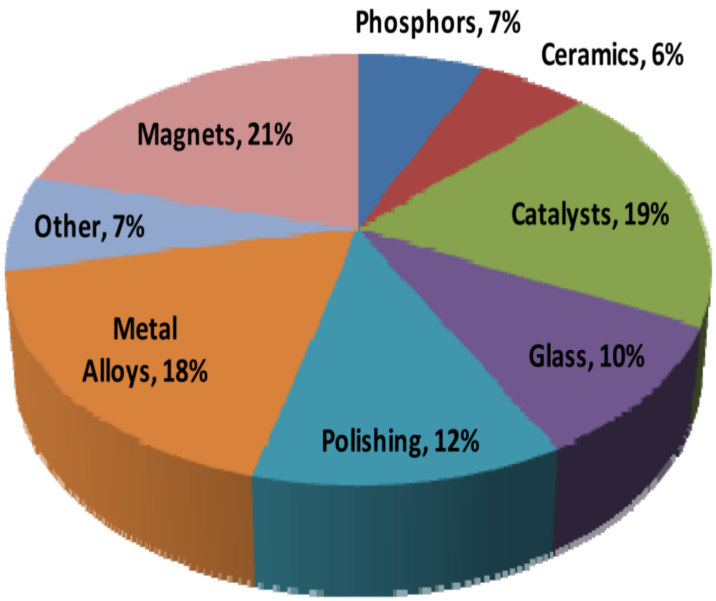
Tb_4O_7

Applications of rare earths

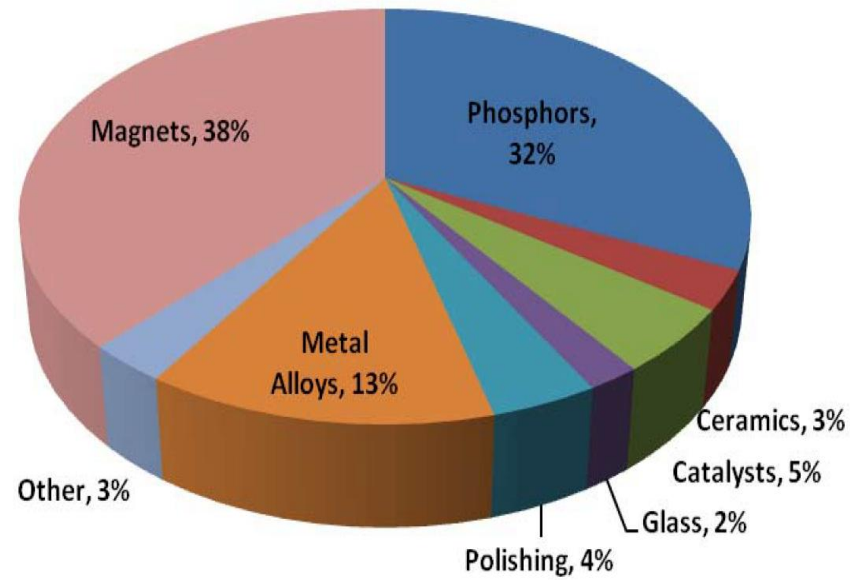


Oxidized state

Applications of rare earths



volume



value

Total volume in 2012: 120,000 tonnes of REO

REEE usage by application

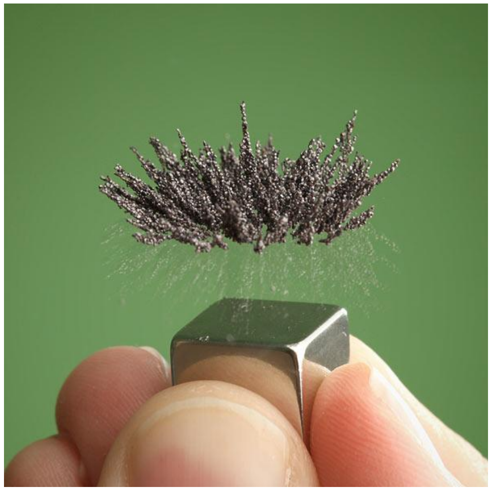
Application	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Other
Magnets			23.4	69.4			2	0.2	5		
Battery alloys	50	33.4	3.3	10	3.3						
Metallurgy	26	52	5.5	16.5							
Auto catalysts	5	90	2	3							
FCC	90	10									
Polishing powder	31.5	65	3.5								
Glass additives	24	66	1	3						2	4
Phosphors	8.5	11				4.9	1.8	4.6		69.2	
Ceramics	17	12	6	12						53	
Others	19	39	4	15	2		1			19	

(source: Lynas Corporation)[8]

Permanent magnets (Nd-Fe-B and Sm-Co)

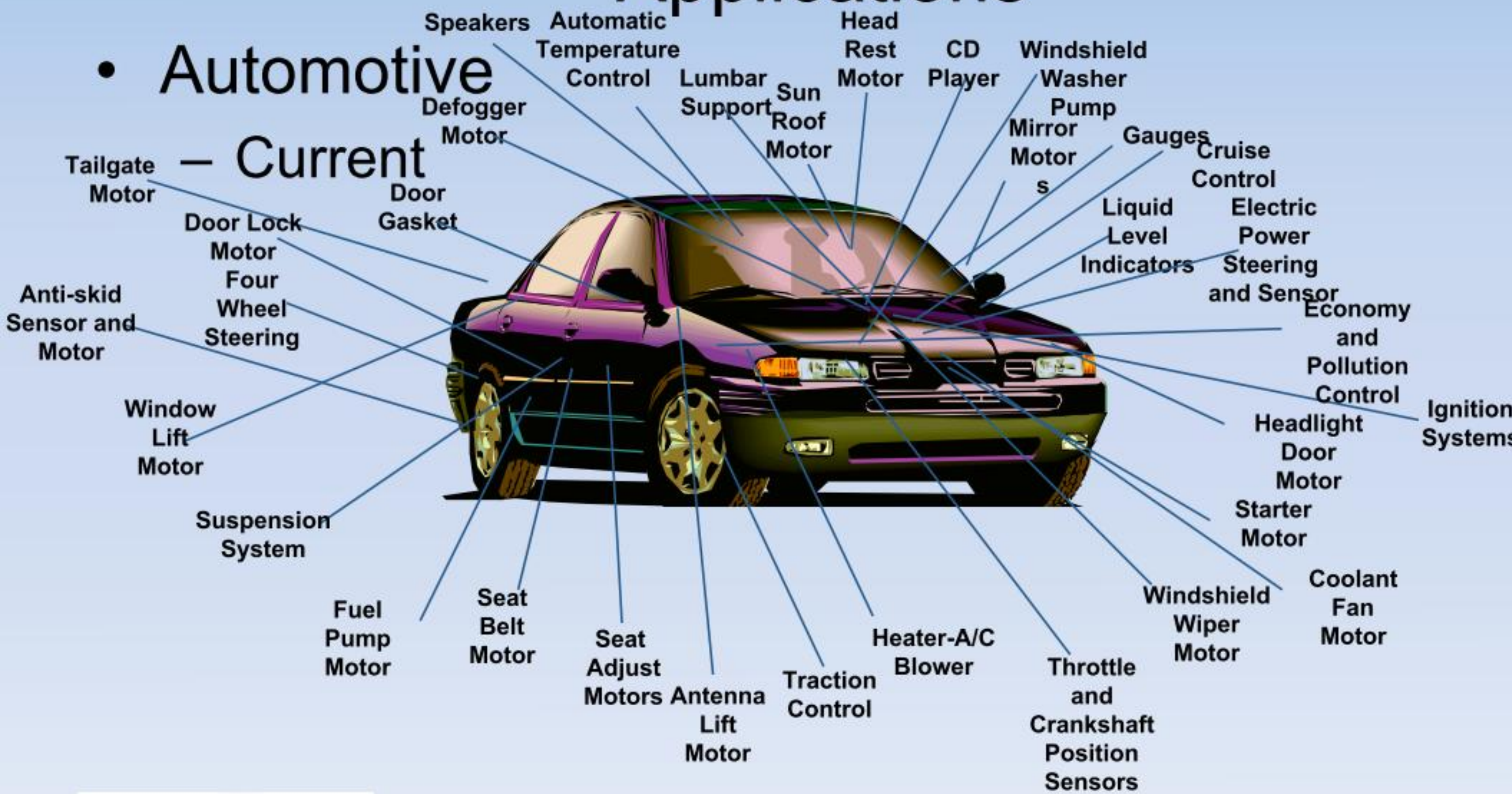
- samarium-cobalt alloys: $SmCo_5$ and Sm_2Co_{17}
  - maximum energy product $(BH)_{max}$:130 to 260 kJ/m^3
  - good corrosion resistance
  - high operating temperatures
  - expensive (Co)
- neodymium-iron-boron alloy: $Nd_2Fe_{14}B$
  - maximum energy product $(BH)_{max}$:512 kJ/m^3
  - poor corrosion resistance (surface plating required)
  - lower operating temperatures (Dy addition)

Permanent magnets (Nd-Fe-B and Sm-Co)



Rare Earth Magnets
Applications

- Automotive
  - Current



Source: Magnequench

Spontaneous Materials

Nickel metal hydride batteries

Positive electrode:

$Ni(OH)_2 + OH^- \leftrightarrows Ni(OOH) + 2H_2 + e^-$

$\rightarrow$: charging

$\leftarrow$: discharging

Negative electrode:

$M + xH_2O + e^- \leftrightarrows MH_x + xOH^-$

$\rightarrow$: charging

$\leftarrow$: discharging

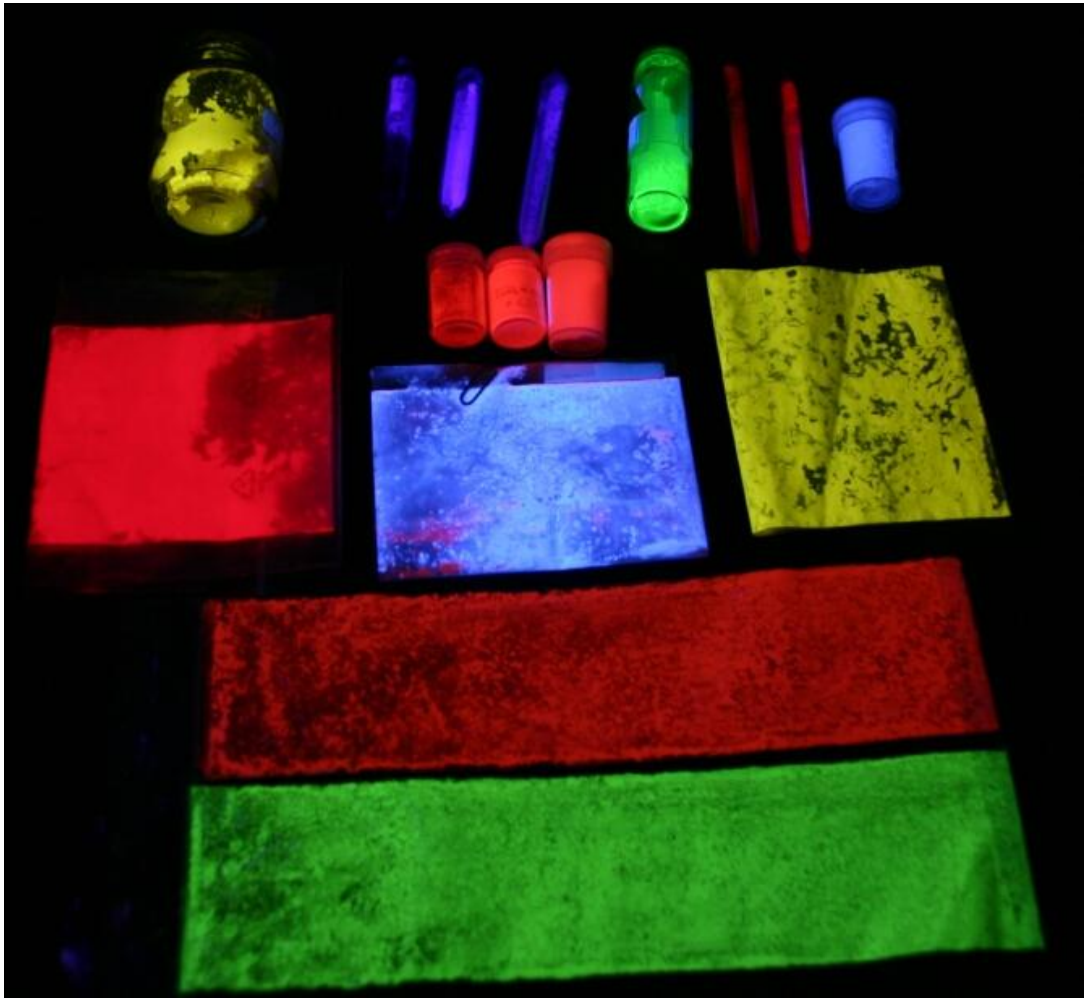
Overall reaction:

$M + xNi(OH)_2 \leftrightarrows xNiOOH + MH_x$

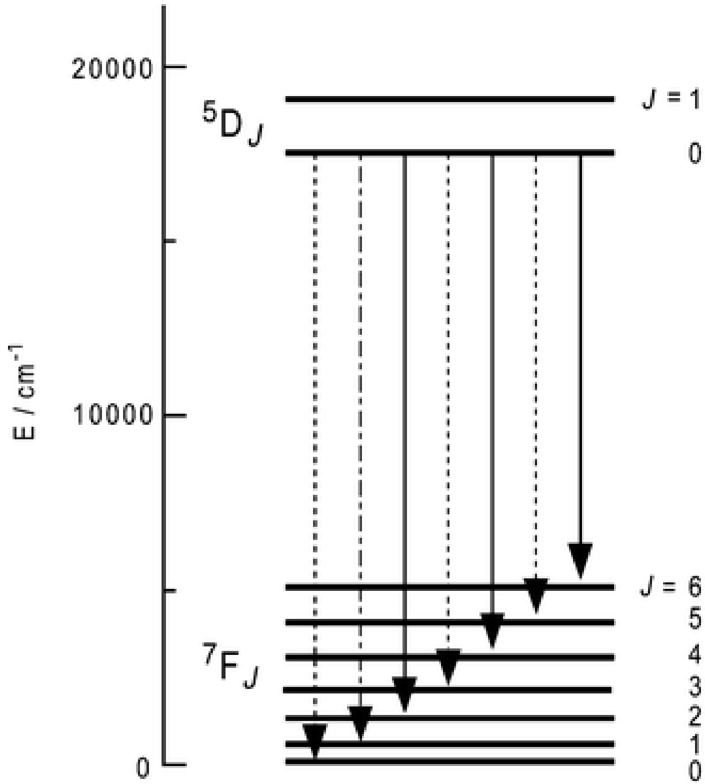
$\rightarrow$: charging

$\leftarrow$: dicharging

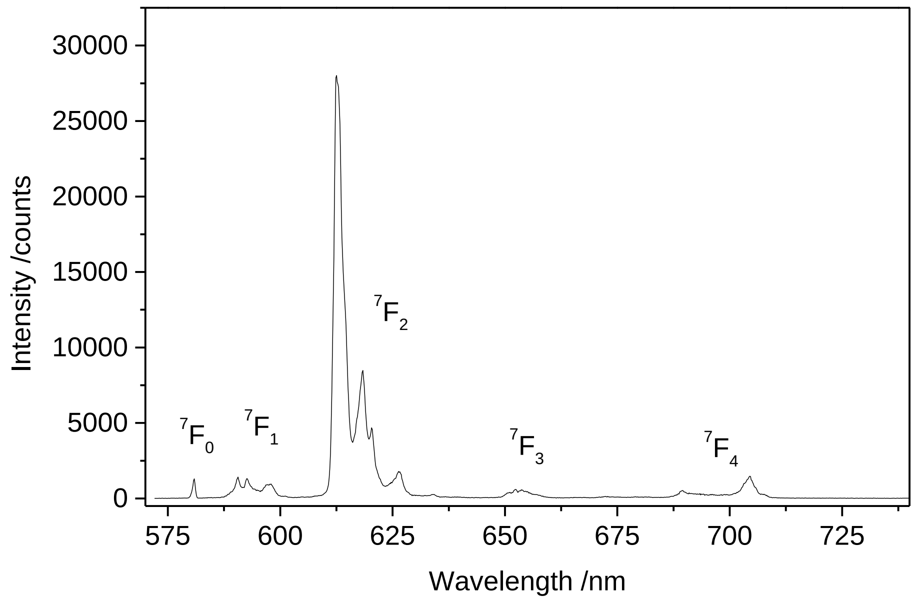
Luminescent materials

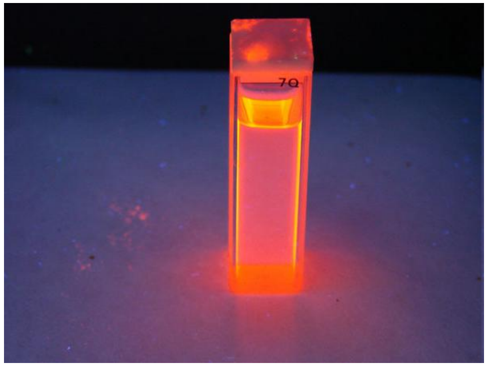


Luminescent materials

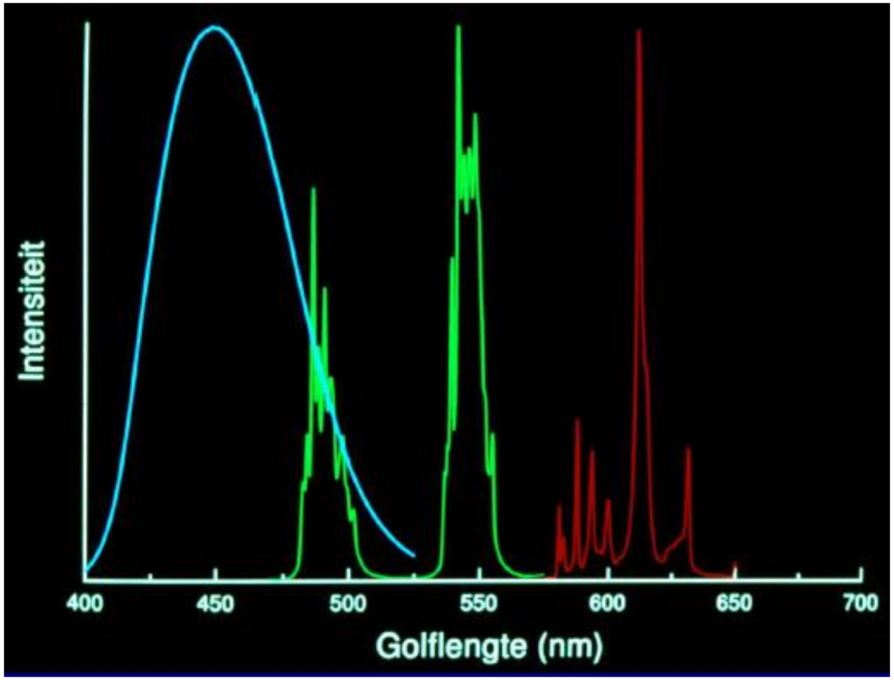


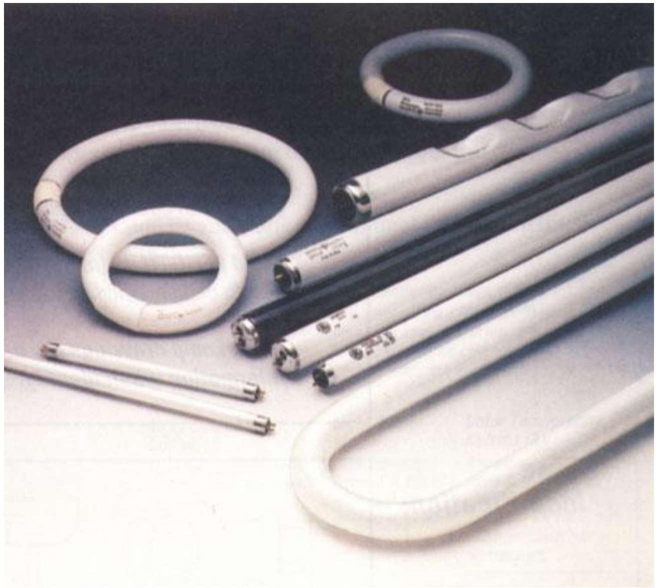
Lowest energy levels of Eu^{3+}



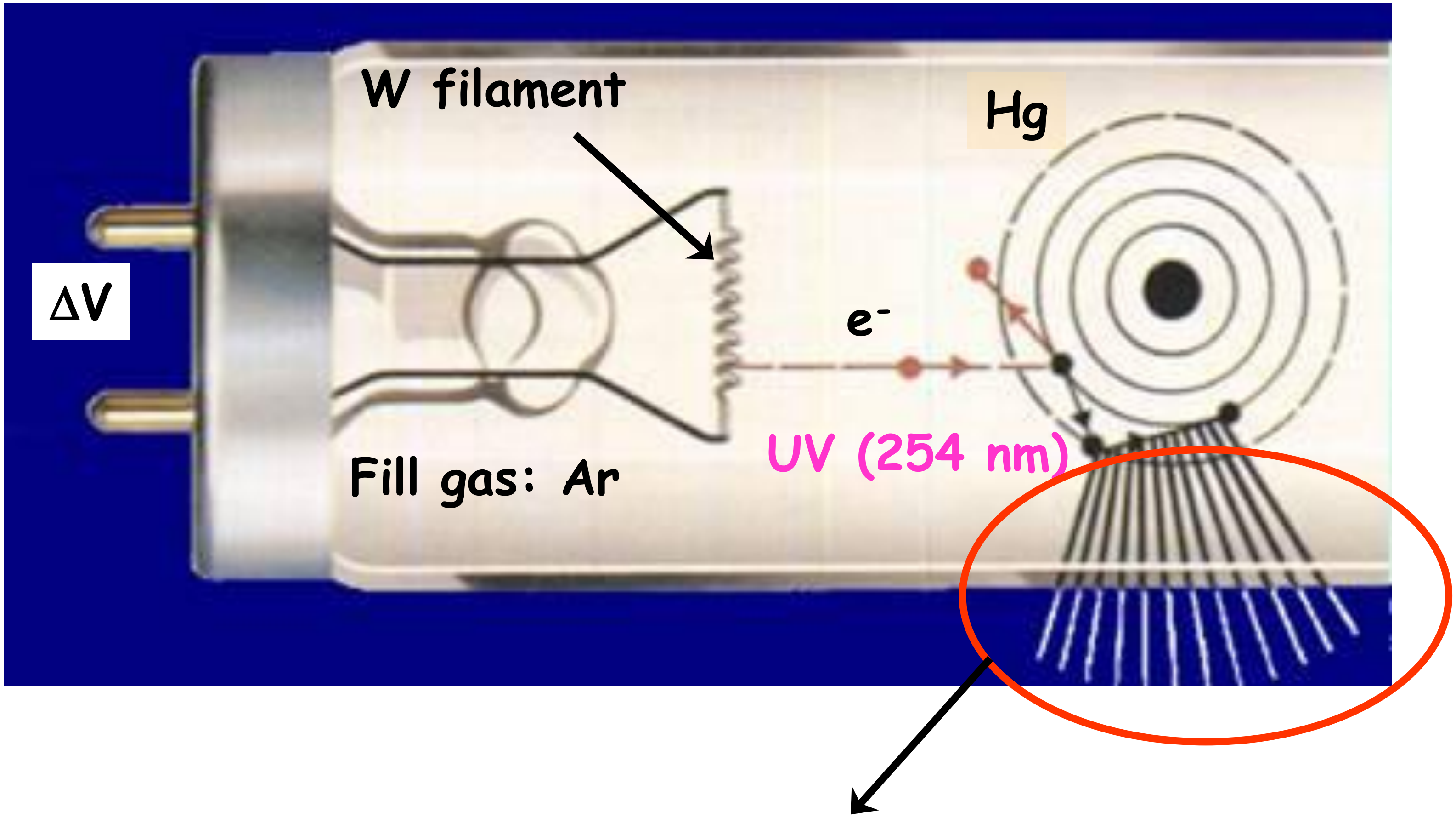


Fluorescent lamps





Fluorescent lamps

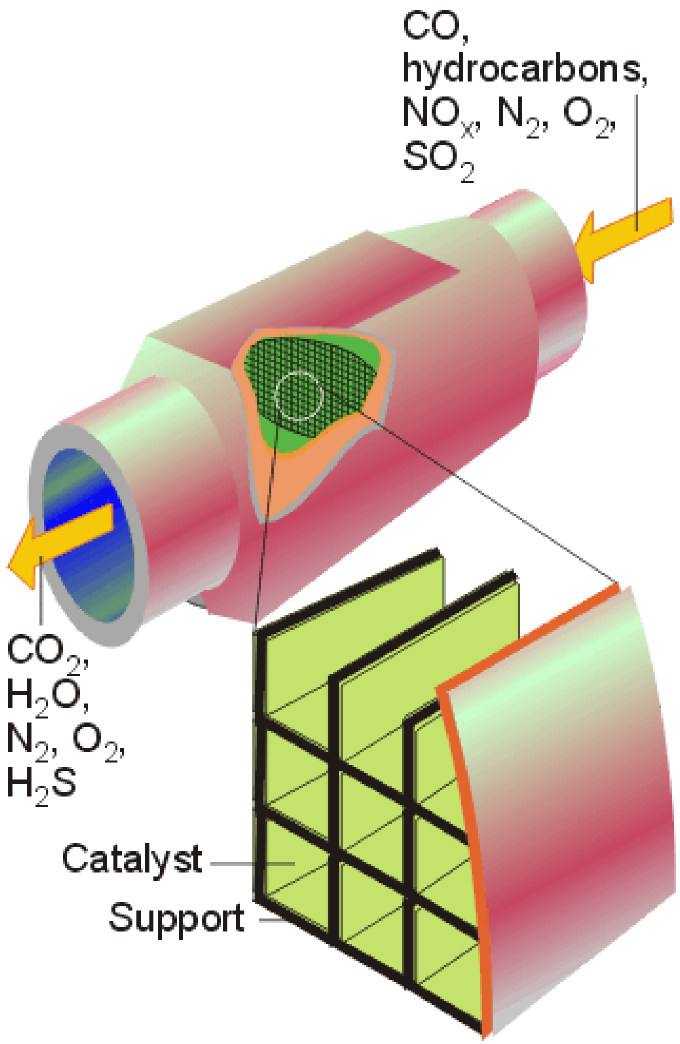


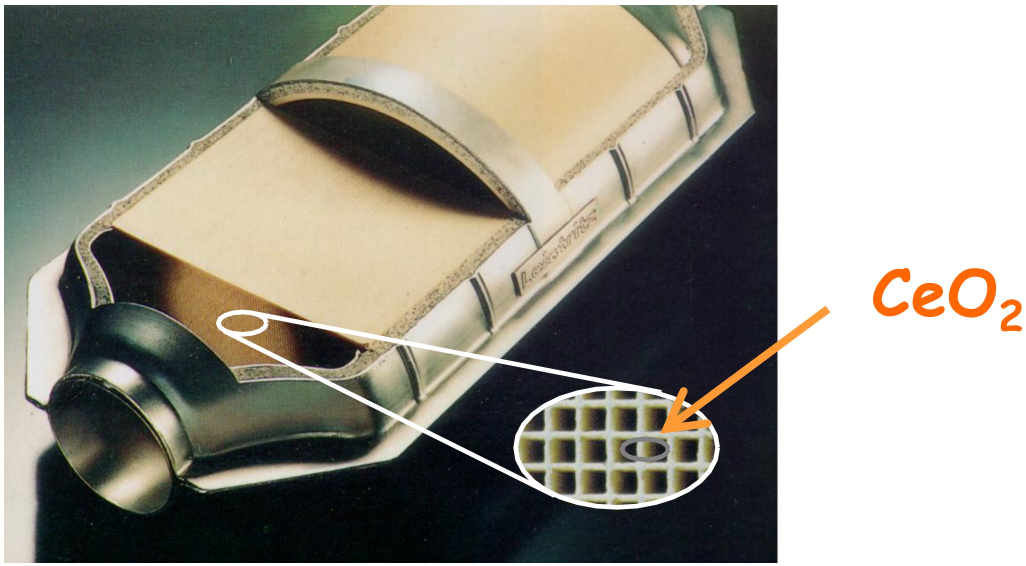
UV photons excite phosphor coating. White light is emitted.

Lamp phosphors

Year	Phosphors		
1960	$Ca_5(PO_4)_3Cl{:}Sb^{3+},Mn^{2+}$ (white)		
1974	$BaMg_2Al_{16}O_{27}{:}Eu^{2+}$	$CeMgAl_{10}O_{19}{:}Tb^{3+}$	$Y_2O_3{:}Eu^{3+}$
1990	$BaMgAl_{10}O_{17}{:}Eu^{2+}$ $(Sr,Ca)_5(PO_4)_3Cl{:}Eu^{2+}$	$(La,Ce)PO_4{:}Tb^{3+}$ $CeMgAl_{10}O_{19}{:}Tb^{3+}$ $(Gd,Ce)MgB_5O_{10}{:}Tb^{3+}$	$Y_2O_3{:}Eu^{3+}$
2005	$BaMgAl_{10}O_{17}{:}Eu^{2+}$	$(La,Ce)PO_4{:}Tb^{3+}$	$Y_2O_3{:}Eu^{3+}$

Automobile exhaust catalysts



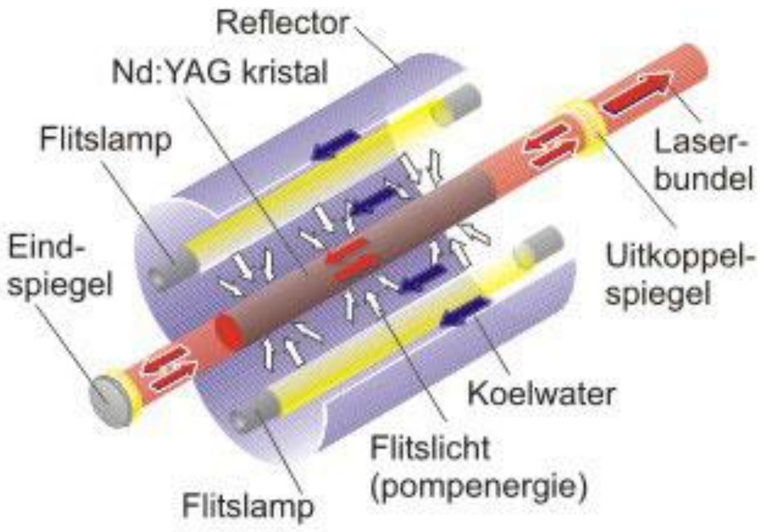


Optical glass

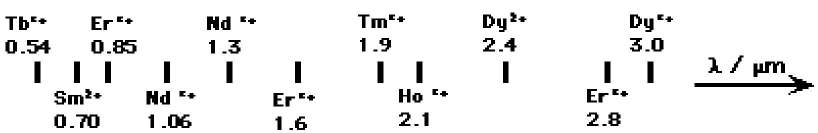
Optical glass for lenses contains up to 40% La_2O_3

(high refractive index and low dispersion)

Laser crystals

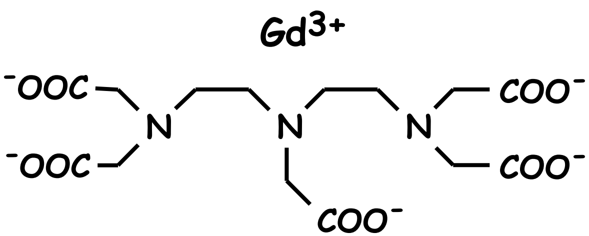


$$YAG = Y_3Al_5O_{12}$$

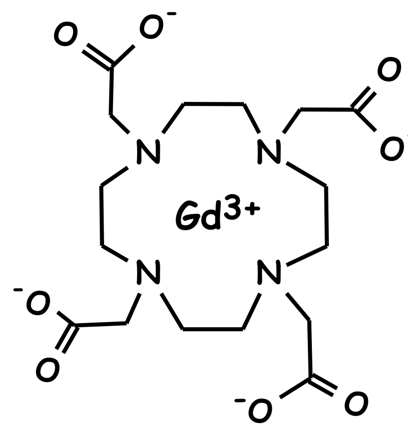


Spectral Range of Rare Earth Lasers

MRI contrast agents



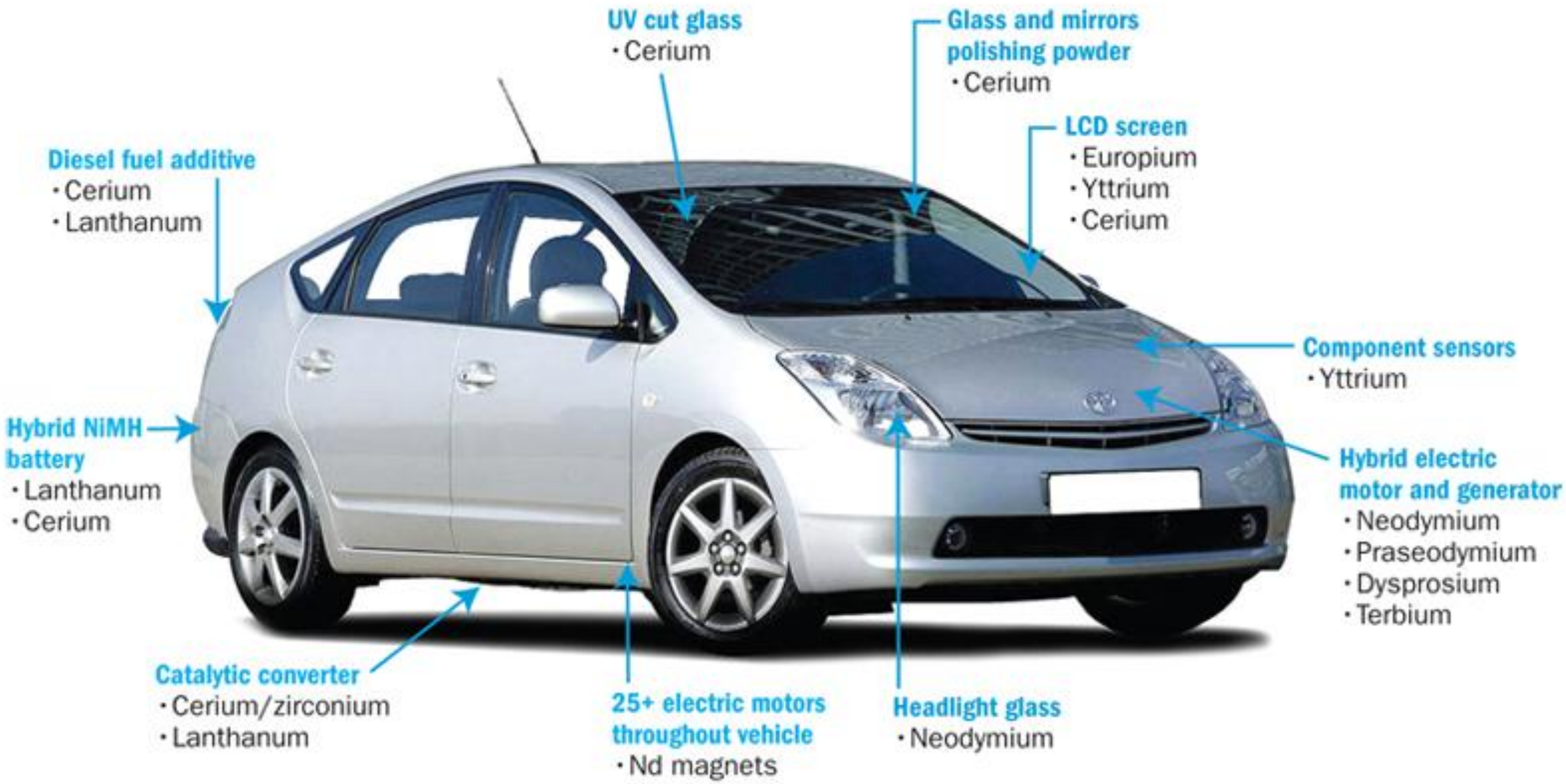
$[Gd(dtpa)]^{2-}$ Magnevist®



$[Gd(dota)]^{-}$

Dotarem®

Rare earths for the car industry



Source: Molycorp

Military applications

F-16 Avionics with REE phosphors

BGM-109 Tomahawk Cruise missile

Nd:YAG designator-rangefinder laser

F-15 with yttria-stabilized zirconia

Useful links

rare3

Research Platform for the
Advanced Recycling and Reuse of Rare Earths

KU LEUVEN

http://kuleuven.rare3.eu/links.php